

REMARKS

Responsive to the Office Action mailed 04 February 2009 and with an extension of time to reply of two months, the present paper is timely filed on or before 06 July 2009, the first day after 04 July 2009 that is not a Saturday, Sunday, or holiday in the District of Columbia.

By the present paper, claims 1 - 13 are amended and no claims are cancelled. Claims 1- 13 are pending in the Application. Reconsideration of the Application in view of the following remarks is respectfully requested.

The Claim Amendments:

Claim 1 is amended to point-out with even greater particularity that which Applicants consider as their invention by expressly reciting that Applicants' inventive phosphors are fluorescence-type phosphors. Support for the amendment can be found in the specification at, for example¹, 7:8-9, 10:30-32, 18:10, and 43:29.

The remaining claims are amended to make them consistent with claim 1 from which the directly or indirectly depend.

Applicants respectfully submit that the amendments do not introduce new matter into the Application.

Claim Rejections Under 35 U.S.C. § 103:

Claims 1, 4 - 7, and 9 were rejected under 35 U.S.C. § 103(a) as allegedly obvious over Shouzo Oshio et al., United States Patent 6,096,243 (Oshio) in view of Akiyama Morihito et al., JP 2000-144129 (Morihito et al.). Because the skilled artisan of the day would not have had a reasonable expectation that an activator or similar material that worked with the type of phosphors disclosed

¹ References to the specification are given as x:y, where x is the page number and y is the line number.

by Morihito et al would work in the type of phosphors of the present invention, Applicants respectfully traverse.

The phosphors disclosed by Morihito et al. and the phosphors of the present invention are fundamentally different, especially with regard to their luminescence decay characteristics. The luminescence decay characteristics of a phosphor are extremely important in determining the suitability of the phosphor for use in a display device ("PDP").

The phosphors disclosed by Morihito et al. and the phosphors of the present invention have strikingly different luminance characteristics. The phosphors of the present invention emit light (luminesce) based on a "fluorescence" phenomenon. One characteristic of fluorescence is that luminance intensity quickly decreases to zero as soon as UV irradiation (excitation) is stopped. As depicted in Fig. 1 below, light emission ("afterglow") stops in 10 milliseconds after irradiation stops. Because of such rapid luminescence decay, fluorescent-type phosphors are especially well suited for use in display devices (PDPs). Prolonged afterglow from a phosphor in a display leads to poor distinctness of displayed images. Short afterglow time is a clearly preferred characteristic for phosphors used in display devices.

Applicants specifically describe their inventive phosphors as fluorescence-type phosphors at, for example, 7:8-9, 10:30-32, 18:10, and 43:29. The luminescence characteristics of Applicants' inventive phosphors were measured with a fluorescence spectrophotometer, *see* 19:34, which *per force* measures fluorescence characteristics.

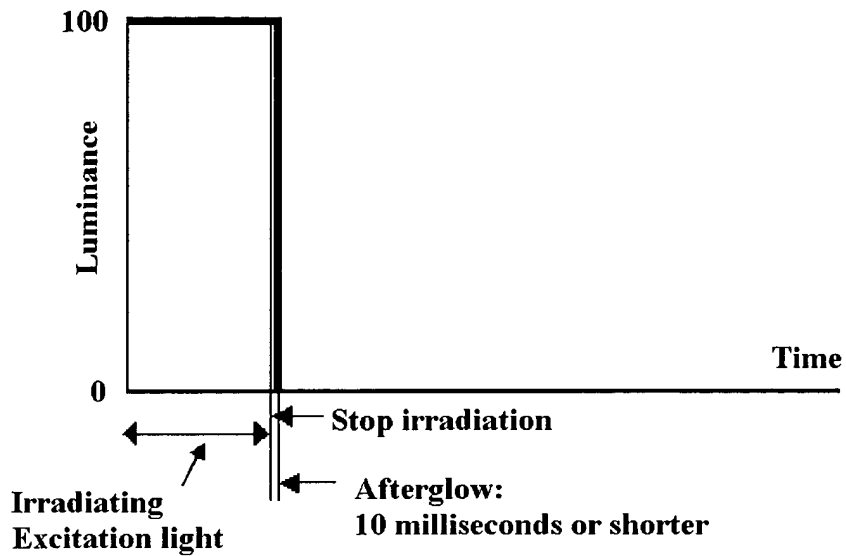


Fig. 1 Fluorescence of a phosphor for a display

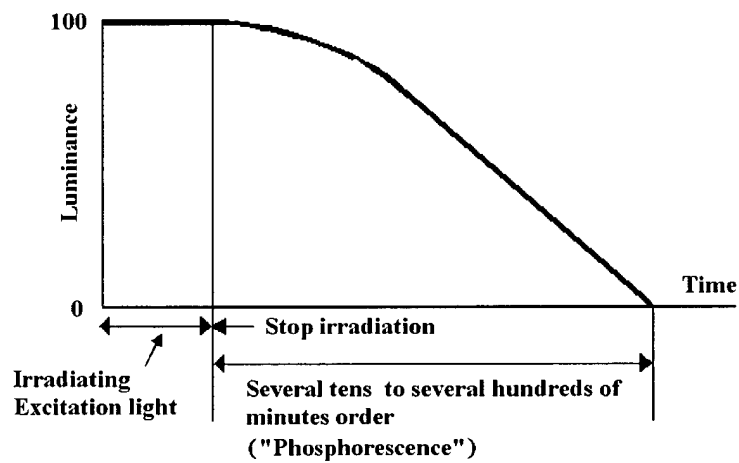


Fig. 2 Phosphorescence in a phosphors for a phosphorescent pigment

On the other hand, as illustrated in Fig. 2, phosphorescence generally continues for a relatively longer period of time, occasionally for several tens of minutes or longer; as much as a day after irradiation (excitation) is terminated. This long afterglow makes phosphorescence-type phosphors unsuitable for use in high-performance PDPs.

The substantial differences between fluorescence-type and phosphorescence-type phosphors are even more fully described in Attachment A, Phosphor Handbook, 83 - 97 (William M. Yen et al., eds., CRC Press, 2nd ed.).

The luminance behavior of the phosphor of Morihito et al. phosphor is plainly attributable to a "phosphorescence" phenomenon. In fact, luminance of the phosphors of Morihito et al. continued for 200 minutes or longer as can be seen in Fig.2 of JP 2000-1441219. Phosphorescence-type phosphors are usually employed in, e.g., clockfaces, lights, guide signs, and the like. But they are never used in display devices because long afterglow times lead to poor displayed images. Morihito et al. sought to extend even further afterglow time of a phosphorescence-type phosphor (*see* Abstract of JP 2000-144129). The problem addressed by Morihito is totally opposite to that addressed by the present invention.

As explained above, the phosphor of the present invention is different from the phosphor disclosed by Morihito et al. in luminance behavior and technical fields of use. For at least this reason, Applicants respectfully submit that a person skilled in the art seeking to develop improved fluorescence-type phosphors would never have looked to Morihito et al., which deals with phosphorescence-type phosphors, for guidance in selecting activators and other components. But the phosphors of the present invention and the phosphors of Morihito et al. differ in still other ways.

In the present invention, the element “(e)” of claim 1 contributes to improved durability. Alkaline earth metal aluminate phosphors containing bivalent europium as an activator generally deteriorate and decrease in luminance after prolonged exposure to elevated temperatures or ultraviolet radiation. Applicants have unexpectedly discovered that element “(e)” serves to prevent deterioration of luminance caused by heat, oxidation, or ultraviolet radiation. The effect is demonstrated in the examples of the instant specification (*see* Tables 1 to 5). As a result, a display device containing the phosphors of the present invention will work for a longer period without deterioration of luminance.

On the other hand, Morihito et al. recites: “[a]ddition of an activator and a coactivator to the above base material dramatically enhances afterglow and luminance” (paragraph [0010] in JP 2000-144129 (emphasis provided)). Thus, the effect of the ‘coactivator’, which can be Nb, is to enhance afterglow and luminance in phosphorescence phenomenon. Morihito et al. is silent about durability-improving effects of a coactivator in a fluorescent phosphor. Nothing in Morihito et al. suggests the totally unexpected stabilizing effect of, e.g., niobium in fluorescence-type phosphors. Moreover, the disclosure in Morihito et al. that addition of e.g. Nb increases afterglow time would have directed the skilled artisan seeking to develop phosphors for use in displays away from use of Nb in phosphors because increased phosphor afterglow is undesirable in displays.

Because nothing in Morihito et al. would have suggested to the skilled artisan of the day to use the coactivators of Morihito et al. in fluorescence-type phosphors and further because Applicants were the first to surprisingly discover that inclusion of, e.g., Nb in fluorescence-type phosphors improves the durability of the phosphors, Applicants respectfully submit that the invention

of claims 1, 4 - 7, and 9 is nonobvious over Oshio et al. in view of Morihito et al. and that the rejection is therefore improper and should be withdrawn.

Claims 2, 3, 8, and 10 - 13 were rejected under 35 U.S.C. § 103(a) as allegedly obvious over Oshio et al. in view of Morihito et al. and further in view of Andre C. Bouchard et al., United States Patent 3,753,759 (Bouchard et al.). Applicants respectfully traverse.

Claims 2, 3, 8, and 10 - 13 depend from claims that, Applicants respectfully submit, contain patentable subject matter. Accordingly, claims 2, 3, 8, and 10 - 13 *per jure* contain patentable subject matter. For at least this reason, Applicants respectfully submit that the rejection is improper and should be withdrawn.

Conclusion:

Based on the forgoing amendments and remarks, Applicants respectfully submit that the claims are now in condition for allowance, which allowance is earnestly solicited. If, in the opinion of the Examiner, a telephone conference would advance prosecution of the application, the Examiner is invited to telephone the undersigned attorneys.

PETITION FOR EXTENSION OF TIME

Applicants hereby petition for an extension of time of TWO MONTHS under 37 C.F.R. § 1.136(a)(1). The fee of \$ 490 required by 37 C.F.R. § 1.17(a) is paid herewith by credit card. Form PTO-2038 accompanies this paper. If form PTO-2038 is missing, cannot be processed, or authorizes payment of an insufficient fee, the Commissioner is hereby authorized to debit Deposit Account 10-1250 for any shortfall.

Conclusion:

Based on the forgoing amendments and remarks, Applicants respectfully submit that the claims are now in condition for allowance, which allowance is earnestly solicited. If, in the opinion of the Examiner, a telephone conference would advance prosecution of the application, the Examiner is invited to telephone the undersigned attorneys.

Respectfully submitted,

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encl. Phosphor Handbook, Attachment A

Second Edition

PHOSPHOR HANDBOOK

Edited by

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Shigeo Shionoya (Deceased)

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CRC Press

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CRC Press is an imprint of the
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chapter two — section seven

Fundamentals of luminescence

Eiichiro Nakazawa

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2.7 Transient characteristics of luminescence

This section focuses on transient luminescent phenomena, that is, time-dependent emission processes such as luminescence after-glow (phosphorescence), thermally stimulated emission (thermal glow), photo (infrared)-stimulated emission, and photoquenching. All of these phenomena are related to a quasistable state in a luminescent center or an electron or hole trap.

2.7.1 Decay of luminescence

Light emission that persists after the cessation of excitation is called *after-glow*. Following the terminology born in the old days, luminescence is divided into fluorescence and phosphorescence according to the duration time of the after-glow. The length of the duration time required to distinguish the two is not clearly defined. In luminescence phenomena in inorganic materials, the after-glow that can be perceived by the human eye, namely that persisting for longer than 0.1 s after cessation of excitation, is usually called phosphorescence. Fluorescence implies light emission during excitation. Therefore, fluorescence is the process in which the emission decay is ruled by the lifetime (<10 ms) of the emitting state of a luminescence center, while the phosphorescence process is ruled by a quasistable state of a center or a trap.

In organic molecules, fluorescence and phosphorescence are distinguished by a quite different definition. The two are distinguished by whether the transition to emit light is

allowed or forbidden by spin selection rules. Light emission due to an allowed transition is called *fluorescence*, while that due to a forbidden transition, usually showing a long after-glow, is called *phosphorescence* (see 2.5).

2.7.1.1 Decay of fluorescence

The decay process of the luminescence intensity $I(t)$ after the termination of excitation at $t = 0$ is generally represented by an exponential function of the elapsed time after the excitation.

$$I(t) = I_0 \exp(-t/\tau) \quad (120)$$

where τ is the decay time constant of the emission. It should be noted that the emission decay curve of nonlocalized centers, donor-acceptor pairs for example, is not always represented in the exponential form of Eq. 120. (See 2.4.)

If one denotes the number of excited luminescence centers in a unit volume by n^* , and the radiative and nonradiative transition probabilities by W_R and W_{NR} , respectively, then the rate equation for n^* is:

$$\frac{dn^*}{dt} = -(W_R + W_{NR})n^* \quad (121)$$

and the solution of this equation is:

$$n^*(t) = n_0^* \exp[-(W_R + W_{NR})t] \quad (122)$$

Here, n_0^* is the value at $t = 0$, that is, at the end-point of excitation or, in other words, at the start point of the after-glow.

Therefore, the lifetime of the center, which corresponds to the elapsed time for n^* to be decreased by the factor of e^{-1} of n_0^* , is $(W_R + W_{NR})^{-1}$. Since the emission intensity is proportional to n^* , the decay time of the after-glow in Eq. 120 is equal to the lifetime of the center:

$$\tau = (W_R + W_{NR})^{-1} \quad (123)$$

and the luminescence efficiency of the center is given by:

$$\eta = \frac{W_R}{W_R + W_{NR}} \quad (124)$$

The radiative transition probability W_R of an emitting state is the summation of the spontaneous emission probability $A_{m \rightarrow n}$ from the state m to all the final states n , (see Eq. 29)

$$W_R = \sum_n A_{m \rightarrow n} = \sum_n \frac{1}{\tau_{mn}} \quad (125)$$

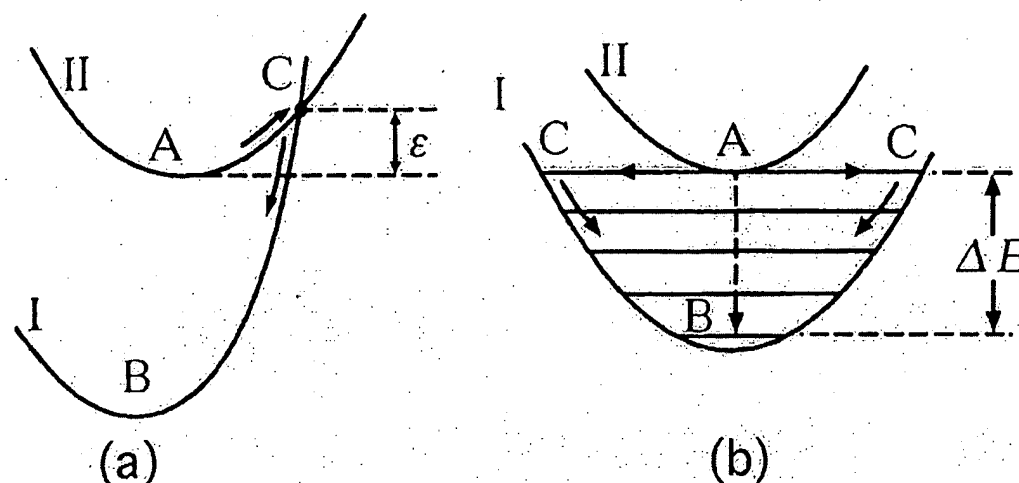


Figure 46 Configurational coordinate models of nonradiative relaxation processes: thermal activation type (a), and multiphonon type (b).

where τ_{mn} is given by Eqs. 32 or 35. The ratio of the transition probability to a particular final state n to W_R , $A_{m \rightarrow n}/W_R$, is called the *branching ratio*.

While the nonradiative transition probability W_{NR} is generally ruled by thermal relaxation processes (i.e., the emission of energy into lattice vibrations), it is also increased by the effect of resonant energy transfer between optical centers. (See 2.8.1.)

The thermal relaxation in a luminescence center can be divided into two types of mechanisms as shown by the two configurational coordinate diagrams (a) and (b) in Figure 46. In the first type (a), the center is thermally activated from point A, the point of the lowest energy on the excited state II, to the crossing point C where the electronic states of the excited and ground states are intermixed, and then thermally released from C to B on the ground state I. The energy ϵ necessary to excite the center from A to C is called the *thermal activation energy*. The probability that the center will make the transition from state II to state I by thermal activation via point C is generally given by:

$$a = s \exp\left(\frac{-\epsilon}{kT}\right) \quad (126)$$

Therefore, the nonradiative transition probability by thermal activation is given by:

$$W_{NR} = a_{II \rightarrow I} = s \exp\left(\frac{-\epsilon}{kT}\right) \quad (127)$$

where k is the Boltzmann constant and s is the frequency factor. This type of nonradiative transition is strongly dependent on temperature, resulting in thermal quenching, that is, the decrease of emission efficiency and shortening of the emission decay time at high temperature (see Eqs. 123 and 124).

An example of the thermal quenching effect is shown in Figure 47 for $\text{Y}_2\text{O}_3\text{:Yb}^{3+}$. The emission from the charge-transfer state (CTS) of Yb^{3+} ions at 530 nm is strongly reduced by thermal quenching at high temperature. The $4f$ emission under CTS excitation (313 nm), however, is increased at high temperature due to the increased amount of excitation transfer from the CTS. The Figure also shows that, as expected, the emission from the

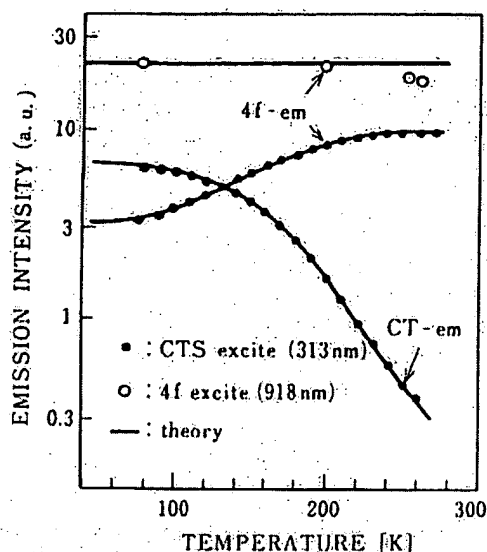


Figure 47 Temperature dependence of two types of the emission in $\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+}$, from the CTS (charge-transfer state) and from a 4f-emitting level of Yb^{3+} ions. (From Nakazawa, E., *J. Luminesc.*, 18/19, 272, 1979. With permission.)

4f level at 930 nm is not so thermally quenched under direct 4f excitation into the emitting level (918 nm).

The second type of nonradiative transition is a multiphonon process shown in Figure 46b. This type is often observed in the relaxation between the 4f excited levels of rare-earth ions, where no cross-point exists between curves I and II in the configuration coordinate diagram because of the similarity of the electronic states. The transition between states I and II occurs at point A, where an energy gap ΔE exists between the states; namely, the transition from the pure electronic state of II to the electron-phonon-coupled state of I with n phonons takes place at A, which is followed by the instantaneous transfer to point C and relaxation to B. The nonradiative transition probability is, therefore, dependent on ΔE or n , the number of phonons necessary to fill the energy gap, since $\Delta E = n \omega_p$, where ω_p is the largest phonon energy. The nonradiative multiphonon transition probability is then given by:²

$$W_{NR}(\Delta E) = W_{NR}(0)e^{-\alpha\Delta E} \quad (128)$$

where α depends on the character of the phonon (lattice vibration). Since the process is mainly due to the spontaneous emission of phonons, the temperature dependence of the probability is small. An experimental result² showing the applicability of Eq. 128 is shown in Figure 48.

2.7.1.2 Quasistable state and phosphorescence

If one of the excited states of a luminescent center is a quasistable state (i.e., an excited state with very long lifetime), a percentage of the centers will be stabilized in that state during excitation. After excitation has ceased, after-glow is caused by the thermal activation of the state. This situation is illustrated using the configurational coordinate diagram in Figure 49, where state III is a quasistable state and state II is an emitting state with a radiative transition probability W_R . The center, once stabilized at A', transfers from state III to state II by thermal activation via point C. The probability of this activation, $a_{III \rightarrow II}$, is given by Eq. 126. Then, if $W_R \gg a_{III \rightarrow II}$, the decay time constant of the emission becomes

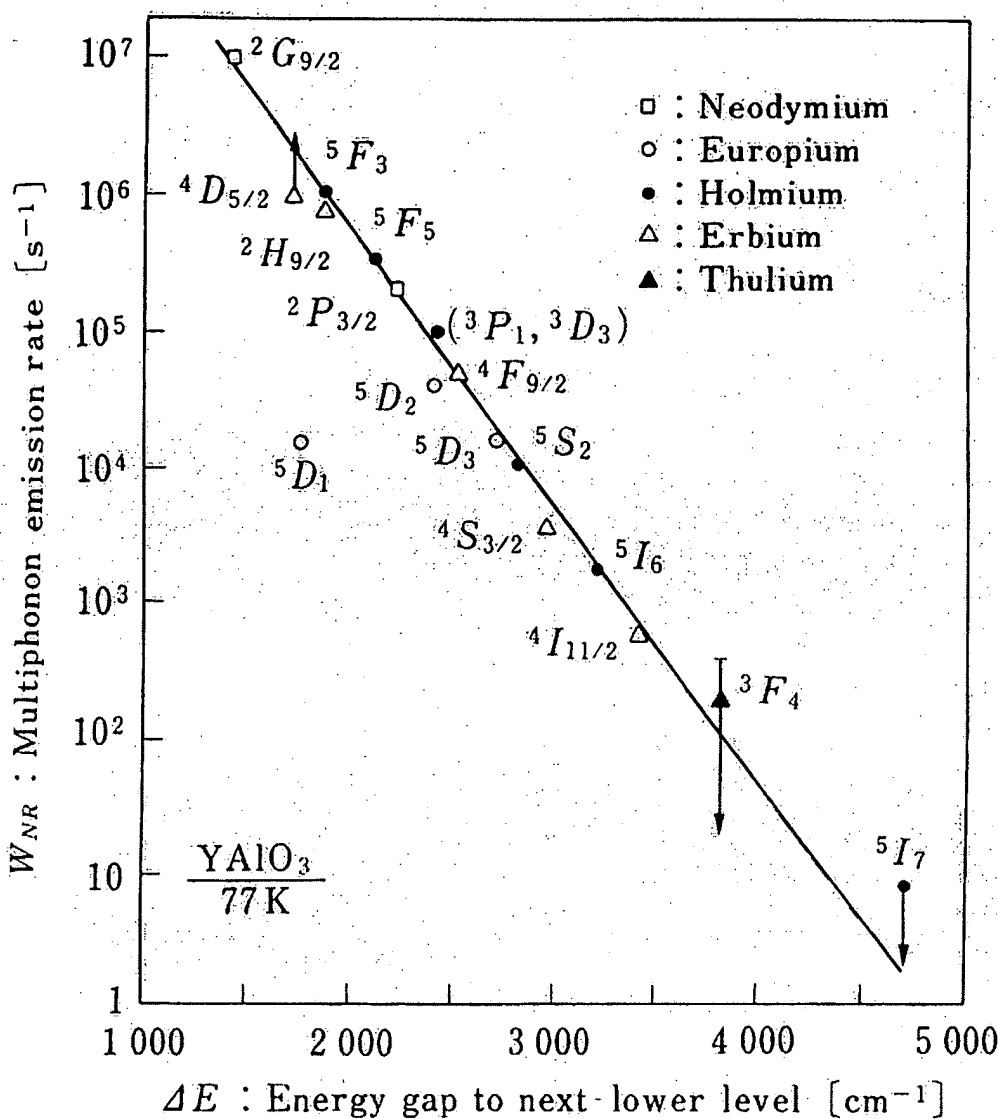


Figure 48 Energy gap law of nonradiative relaxation due to multiphonon processes. (From Weber, M.J., *Phys. Rev.*, B8, 54, 1993. With permission.)

almost equal to $1/a_{m \rightarrow n}$, that is, the lifetime of the quasistable state. The decay curve of the after-glow is represented by an exponential function that is similar to Eq. 120, and is strongly temperature dependent. The decay time constant of an emitting center with quasistable states is not usually longer than a second.

2.7.1.3 Traps and phosphorescence

Excited electrons and holes in the conduction and valence bands of a phosphor can often be captured by impurity centers or crystal defects before they are captured by an emitting center. When the probability for the electron (hole) captured by an impurity or defect center to recombine with a hole (electron) or to be reactivated into the conduction band (valence band) is negligibly small, the center or defect is called a *trap*.

The electrons (holes) captured by traps may cause phosphorescence (i.e., long after-glow) when they are thermally reactivated into the conduction band (valence band) and then radiatively recombined at an emitting center. The decay time of phosphorescence

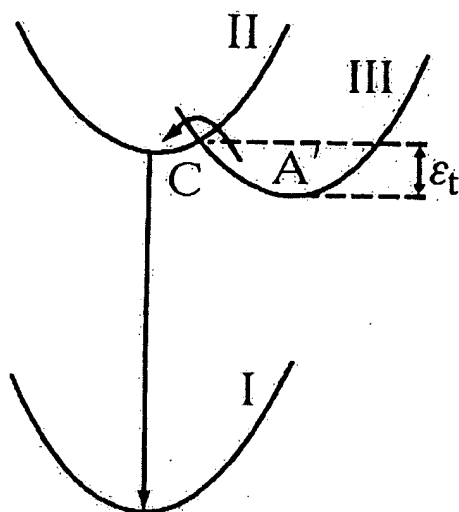


Figure 49 Configurational coordinate model of the luminescence after-glow (phosphorescence) via a quasistable state.

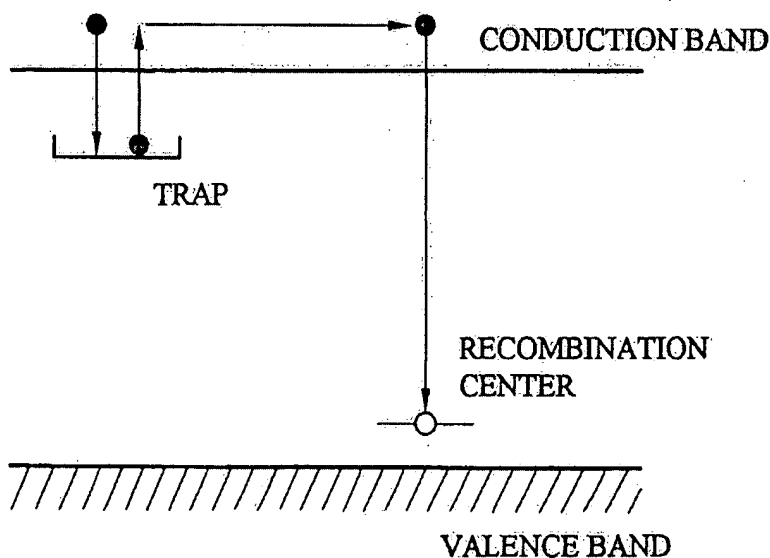


Figure 50 Luminescence after-glow process via a trap in an energy band scheme.

due to traps can be as long as several hours and is often accompanied by photoconductive phenomena.

The decay curve of the after-glow due to traps is not generally represented by a simple exponential function. The form of the curve is dependent on the concentration of the traps and on the electron capture cross-sections of the trap and the emitting center. Furthermore, it also depends on the excitation intensity level.

While several kinds of traps usually exist in practical phosphors, only one kind of electron trap is presumed to exist in the simple model shown in Figure 50. Let N be the trap concentration, and n_c and n_t the number of electrons per unit volume in the conduction band and trap states, respectively. The number of holes, denoted by p is equal to $n_c + n_t$. The rate equation representing the decaying processes of the concentration of electrons and holes after the termination of excitation is:

$$\begin{aligned}\frac{dn_t}{dt} &= -an_t + b(N - n_t)n_c \\ \frac{dp}{dt} &= -rpn_c\end{aligned}\quad (129)$$

where a is the probability per second for a trapped electron to be thermally excited into the conduction band and is given by the same form as Eq. 126 with the density of states in the conduction band included in s . The probabilities that a free electron in the conduction band will be captured by a trap or to recombine with a hole are given by b and r , respectively. It is supposed that the number of the electrons n_c in the conduction band in the after-glow process is so small that $p \approx n_c$ and $dp/dt \approx dn_c/dt$. Then, the above two equations give:

$$\frac{dn_t}{dt} = \frac{-an_t^2}{n_t + (b/r)(N - n_t)} \quad (130)$$

This equation can be solved analytically for two cases: $b \ll r$ and $b \approx r$.

First, the case of $b \ll r$, which presumes that the electrons once released from traps are not retrapped in the after-glow process. Eq. 130 then simplifies to:

$$\frac{dn_t}{dt} = -an_t \quad (131)$$

Since the emission intensity is given by $I(t) \propto dp/dt$, and $dp/dt \approx dn_c/dt$ as mentioned above, then

$$I(t) = I_0 \exp(-at) \quad (132)$$

This simple exponential decay of after-glow is the same as the one due to the quasistable state mentioned previously and is called a first-order or monomolecular reaction type in the field of chemical reaction kinetics.

In the case $b \approx r$, which means that the traps and emitting centers have nearly equal capturing cross-sections, Eq. 130 can be simplified to:

$$\frac{dn_t}{dt} = -\frac{a}{N} n_t^2 \quad (133)$$

and then the number of trapped electrons per unit volume is given by:

$$n_t = \frac{n_{t0}}{1 + (N/an_{t0})t} \quad (134)$$

Approximating $I(t) \propto dn_t/dt$ as before, the decay curve of the after-glow is obtained as:

$$I(t) = \frac{I_0}{(1 + \gamma t)^2}, \quad (\gamma = N/an_{t0}) \quad (135)$$

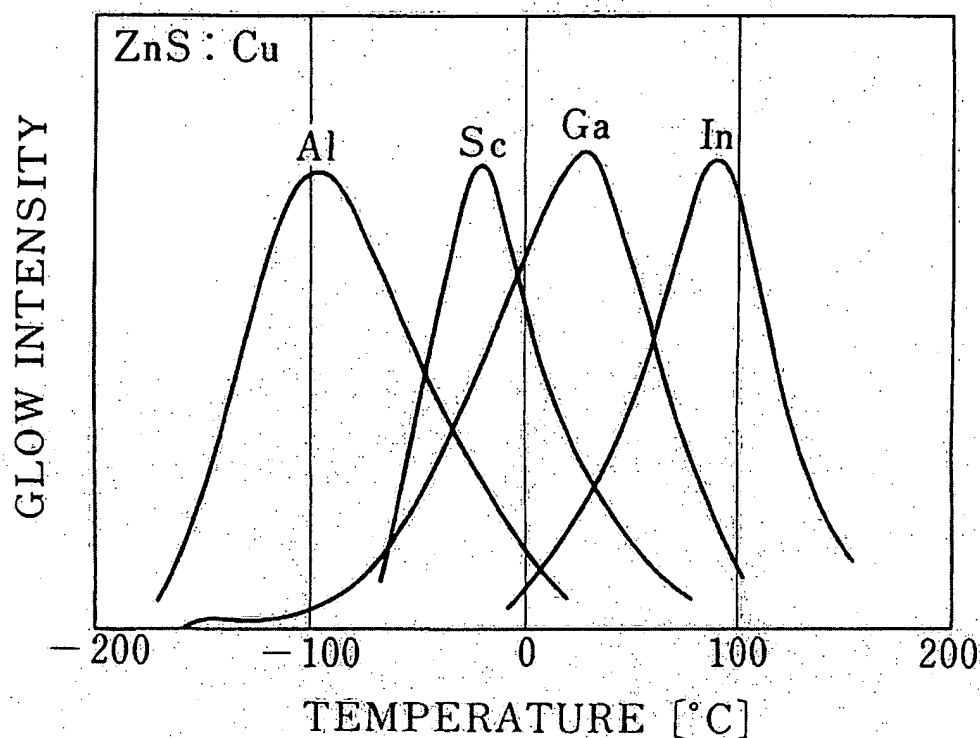


Figure 51 Glow curves of ZnS:Cu phosphors co-activated with Al, Sc, Ga, and In. (From Hoogenstraeten, W., *Philips Res. Rept.*, 13, 515, 1958. With permission.)

This form is called the second-order or bimolecular reaction type, where the decay curve is changed by excitation intensity as well as by temperature.

While the treatise mentioned above is a simple model presuming a single kind of trap, the real phosphors may have several kinds of traps of different depths. In many real cases, therefore, the after-glow decay curve is not represented simply by a monomolecular or bimolecular reaction curve. It often fits into the following equation.

$$I(t) = \frac{I_0}{(1 + \gamma t)^n} \quad (136)$$

where n is around 0.5–2. If $t \gg 1/\gamma$, this decay curve can be approximated by $I(t) \propto t^{-n}$. The decay time constant of an after-glow is therefore denoted either by the $1/e$ decay time or the 10% decay time.

2.7.2 Thermoluminescence

When a phosphor with deep traps is excited for a while at rather low temperatures and then heated, it shows an increased after-glow called thermally stimulated luminescence due to the recombination of electrons thermally reactivated from the deep traps. This emission is also called thermoluminescence, and the temperature dependence of the emission intensity is called the glow curve, which is a good means to measure the depth (i.e., the activation energy of traps). Figure 51 shows the glow curves of ZnS:Cu phosphors with various co-activators.³

The measurement of a glow curve of a phosphor sample proceeds as follows.

1. The sample is cooled to a low temperature (liquid nitrogen is often used as coolant).
2. The sample is excited by UV light until the traps are filled with electrons or holes.
3. The excitation is terminated, and the temperature of the sample is raised at a constant rate, $dT/dt = \beta$, while the intensity is recorded.
4. The temperature dependence of fluorescence is then measured under a constant UV excitation, which is used to calibrate the effect of temperature quenching on the thermoluminescence intensity.

The glow curve thus obtained is analyzed with the following theory. Assume that (1) a single kind of trap exists; (2) the decay of after-glow is of the first-order type given by Eq. 132, and (3) the probability for the trapped electrons to be thermally released into the conduction band is given by Eq. 126. Since the retrapping of the released electrons is neglected in the first-order kinetics, the change in the number of trapped electrons is:

$$\frac{dn_t}{dt} = -n_t \exp(-\epsilon/kT) \quad (137)$$

Integrated from a temperature T_0 to T with the relation $dT/dt = \beta$, this equation gives the number of residual electrons in the traps at T as:

$$n_t(T) = n_{t0} \exp\left(-\int_{T_0}^T \exp\left(\frac{-\epsilon}{kT}\right) \frac{dT}{\beta}\right) \quad (138)$$

where n_{t0} is the number of the trapped electrons at the initial temperature T_0 . Therefore, the emission intensity at T , approximated by $I \propto dn_t/dt$ as mentioned in the previous section, is given by:

$$I(T) \propto n_{t0} \exp\left(\frac{-\epsilon}{kT}\right) \exp\left(-\int_{T_0}^T \exp\left(\frac{-\epsilon}{kT}\right) \frac{dT}{\beta}\right) \quad (139)$$

Based on this equation, the following techniques have been proposed for obtaining the trap depth (activation energy ϵ) from a glow curve.

(a) In the initial rising part of the glow peak on the low-temperature side where the number of trapped electrons is nearly constant, Eq. 139 is approximated by

$$I(T) \propto \exp\left(\frac{-\epsilon}{kT}\right) \quad (140)$$

Then the slope of the Arrhenius plot ($1/T$ vs. $\ln I$) of the curve in this region gives the trap depth ϵ . In fact, however, it is not easy to determine the depth with this method because of the uncertainty in fixing the initial rising portion.

(b) Let the peak position of a glow curve be T_m . Then, the following equation derived from $dI/dT = 0$ should be valid.

$$\frac{\beta\epsilon}{kT_m^2} = \exp\left(\frac{-\epsilon}{kT_m}\right) \quad (141)$$

Table 1

β/s [K]	K [K/eV]	T_n [K]
10^{-4}	833	35
10^{-5}	725	28
10^{-6}	642	22
10^{-7}	577	17
10^{-8}	524	13
10^{-9}	480	10
10^{-10}	441	7
10^{-11}	408	6
10^{-12}	379	6
10^{-13}	353	5
10^{-14}	331	5
10^{-15}	312	4

From Curie, D., *Luminescence in Crystals*, John Wiley & Sons, 1963, chap. VI. With permission.

If the frequency factor s is obtained in some manner, ϵ can be estimated by this relation from the observed value of T_m . Note that the temperature rise rate β should be kept constant throughout the measurement for this analysis. Randall and Wilkins⁴ performed a numerical calculation based on this theory and obtained the following equation, which approximates the trap depth ϵ with 1% error.

$$\epsilon = \frac{T_m - T_0(\beta/s)}{K(\beta/s)} \quad (142)$$

Here, $T_0(\beta/s)$ and $K(\beta/s)$ are the parameters determined by β/s as listed in Table 1.

For ZnS:Cu, $s = 10^9 \text{ s}^{-1}$ is assumed and the following estimations have been proposed for various values of β .⁵

$$\epsilon[eV] = T_m/500 \quad (\beta = 1K/s)$$

$$\epsilon[eV] \approx T_m/400 \quad (\beta = 0.01K/s)$$

$$\epsilon[eV] = (T_m - 7)/433 \quad (\beta = 0.06K/s)$$

(c) If the glow curve is measured with two different rise rates, β_1 and β_2 , it is apparent that one can obtain the value of ϵ without assuming the value of s in Eqs. 141 or 142, using the following equation.

$$\frac{\epsilon}{k} \left(\frac{1}{T_{m2}} - \frac{1}{T_{m1}} \right) = \ln \left(\frac{\beta_1}{\beta_2} \cdot \frac{T_{m2}^2}{T_{m1}^2} \right) \quad (143)$$

Hoogenstraaten³ extended this method for many raising rates β_i , and, by plotting the curves $(1/T_{mi} \text{ vs. } \ln(T_{mi}^2/\beta_i))$, obtained the trap depth from the slope ϵ/k of the straight line connecting the plotted points as shown in Figure 52.⁶ A numerical analysis⁷ has shown that Hoogenstraaten's method gives the best result among several methods for obtaining trap depths from glow curves.

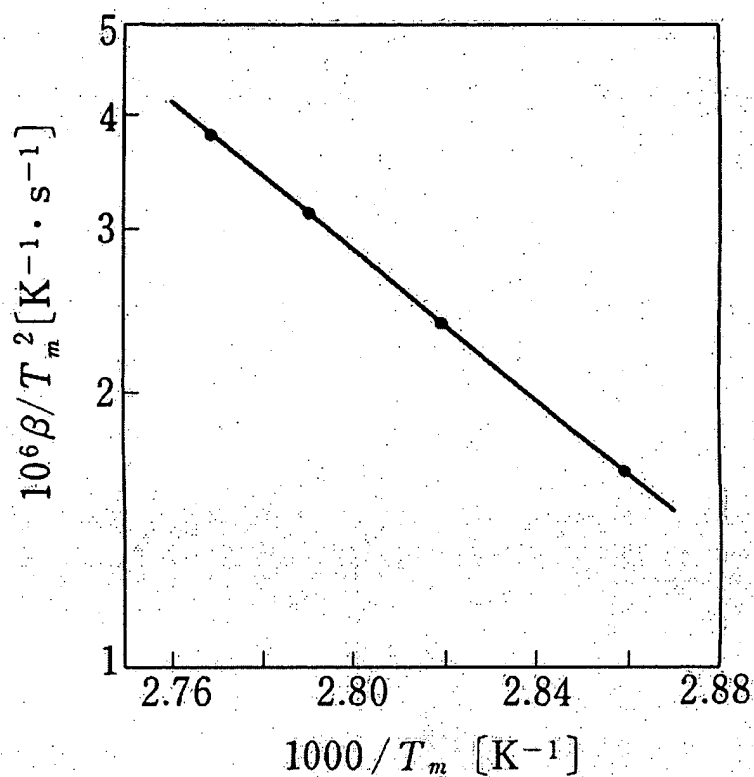


Figure 52 Hoogenstraaten plot showing the dependence of the peak temperature (T_m) of a glow curve on the temperature-raising rate (β). The slope of this line gives the depth (activation energy) of the trap. (From Avouris, P. and Morgan, T.N., *J. Chem. Phys.*, 74, 4347, 1981. With permission.)

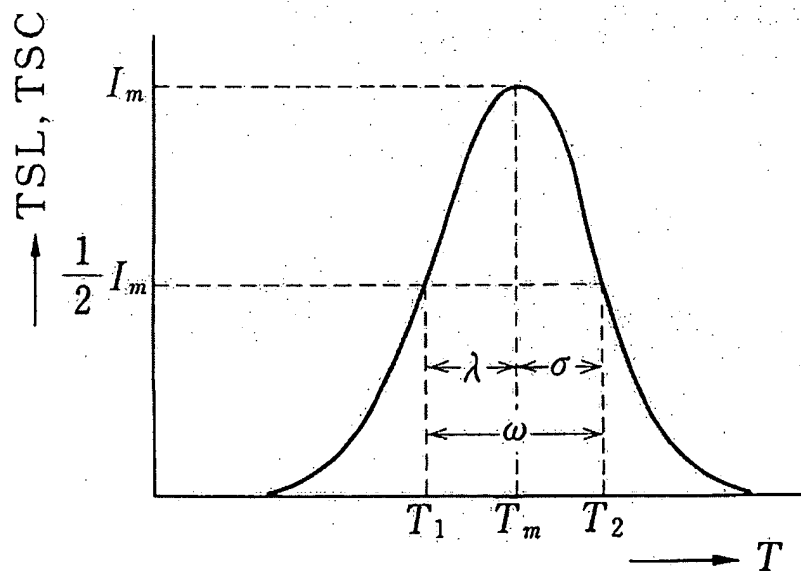


Figure 53 Predicted shape of a glow curve.

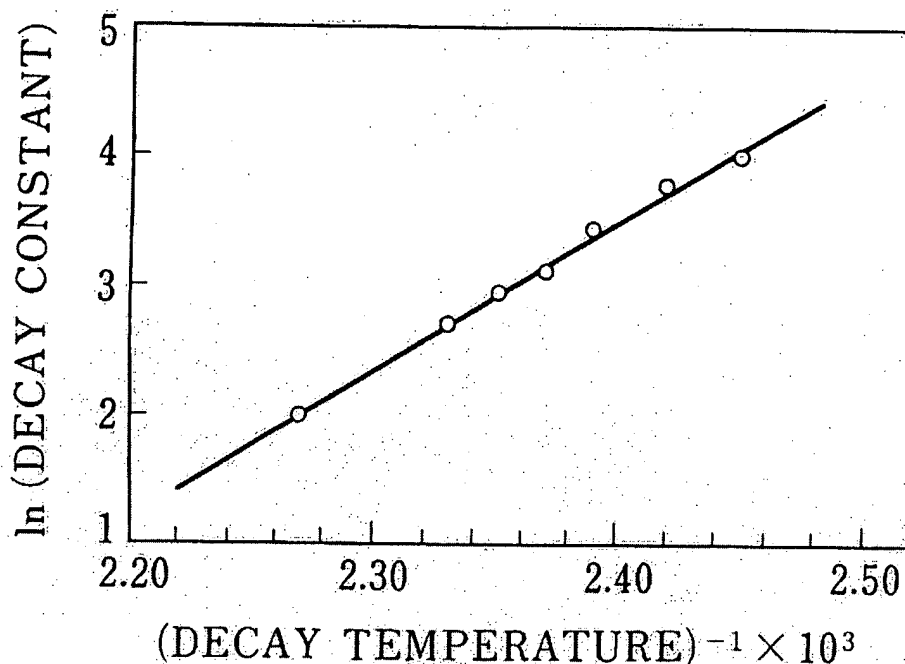


Figure 54 Temperature dependence of the decay time constant of ZnS:Cu. (From Bube, R.H., *Phys. Rev.*, 80, 655, 1950. With permission.)

(d) Many methods for obtaining the depth ϵ from the width of the peak of a glow curve have been proposed.⁵ The results are listed below, where the width for a peak is defined in various ways, as shown in Figure 53.

1. $\epsilon = kT_m^2 \sigma$
2. $\epsilon = 2kT_m(1.25T_m/\omega - 1)$
3. $\epsilon = 1.52 kT_m^2/\lambda - 3.16 kT_m$
4. $\epsilon = (1 + \omega/\lambda)kT_m^2/\sigma$

Note that these methods are usable under certain restricted conditions.⁵

There is a method to obtain trap depth other than the glow-curve method described above. It is to use the temperature dependence of the decay time of after-glow, that is, phosphorescence. As mentioned in relation to Eq. 132, the decay time constant of the exponential after-glow due to the first-order reaction kinetics is equal to the inverse of the thermal detrapping probability, σ^{-1} , and its temperature dependence is given by:

$$\tau_{1/e} = s^{-1} \exp\left(\frac{\epsilon}{kT}\right) \quad (144)$$

Therefore, the trap depth ϵ can be obtained from the measurements of the phosphorescence decay time $\tau_{1/e}$ at several different temperatures (T_i). An example is shown in Figure 54, in which the depth is obtained from the slope of the straight line connecting the Arrhenius plots of the observed values⁸ for τ_i and T_i .

A usable method with which trap depths and relative trap densities are obtained more easily and accurately was recently proposed.⁹ In this method, the sample is excited periodically under a slowly varying temperature and the after-glow (phosphorescence) intensity is measured at several delay times (t_d) after the termination of excitation in each cycle.

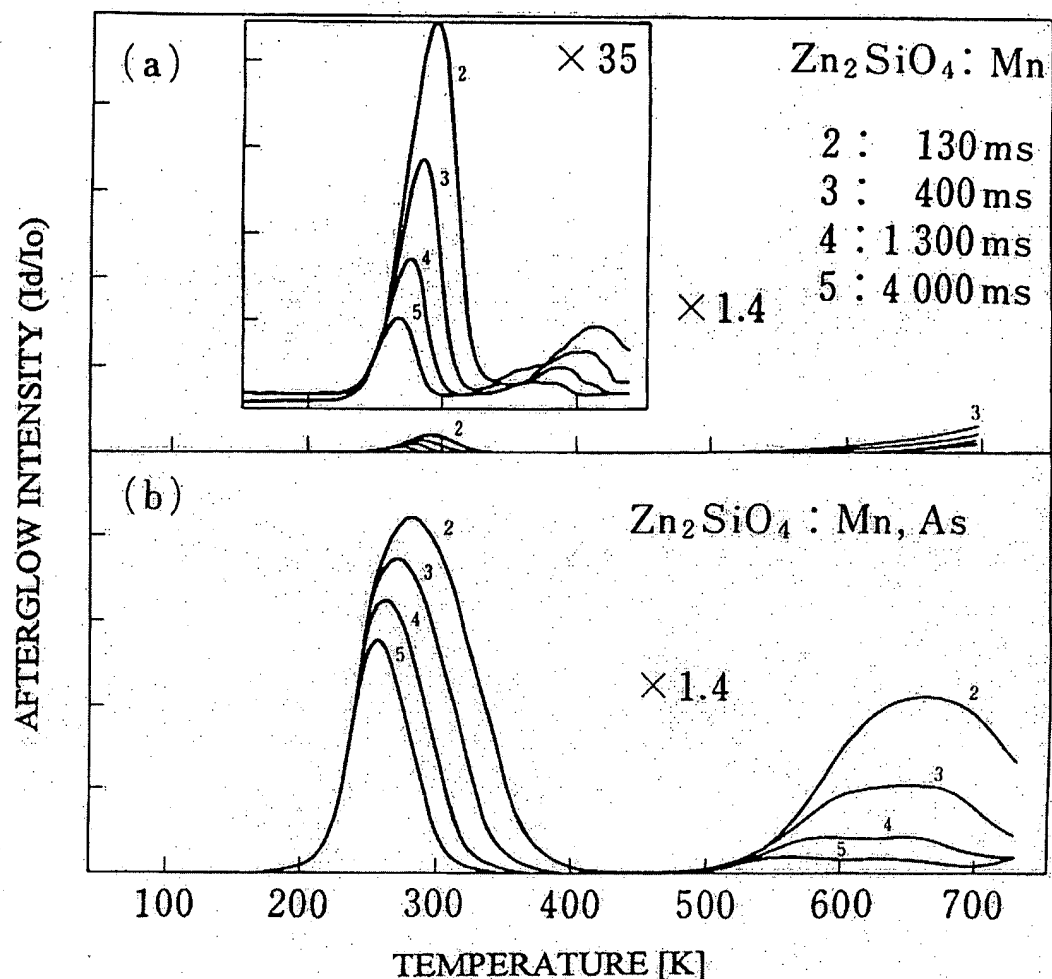


Figure 55 Temperature dependencies of the after-glow intensity of (a) $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and (b) $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}, \text{As}$. The delay time (t_d) is 0.13, 0.4, 1.3, and 4.0 s, respectively, for the curves numbered from 2 through 5 in the figures. (From Nakazawa, E., *Jpn. J. Appl. Phys.*, 23(9), L755, 1984. With permission.)

The temperature dependence of the after-glow intensity at each delay time makes a peak at a certain temperature T_m . From the equation $dI/dT = 0$ and using either Eq. 132 or Eqs. 135 and 136, the following relation is obtained between the peak temperature T_m and the delay time t_d .

$$t_d = s^{-1} \exp\left(\frac{\epsilon}{kT_m}\right) \quad (145)$$

Since Eq. 145 is similar to Eq. 144 (i.e., the decay time method), the method used there for obtaining the trap depth ϵ can be applied hereby, substituting t_d for τ , and T_m for T_f . An example of the measured after-glow intensity curves is shown in Figure 55.

2.7.3 Photostimulation and photoquenching

When a phosphor with deep traps is once excited and then irradiated by infrared (IR) or red light during the decay of its phosphorescence, it sometimes shows photostimulation

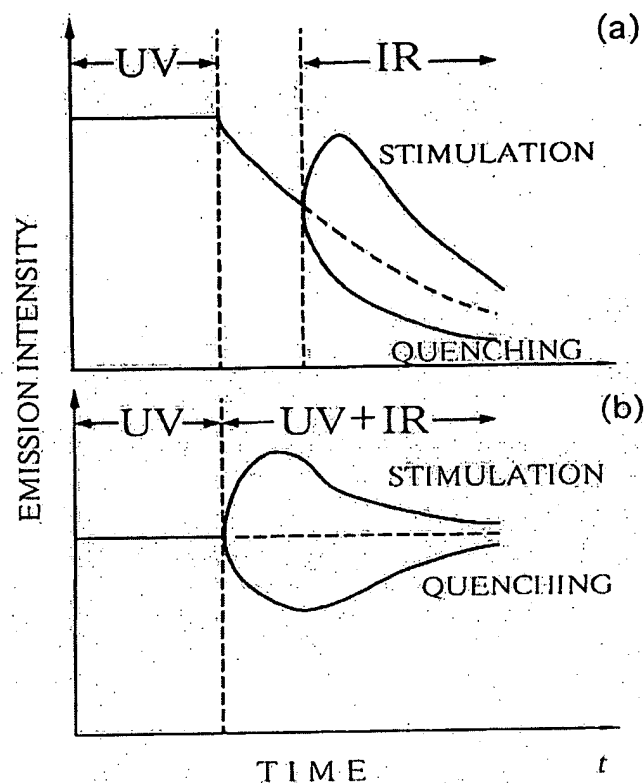


Figure 56 Photostimulation and photoquenching simulation for the case (b) under a constant excitation and (a) in the after-glow process after the termination of excitation.

or photoquenching of luminescence; that is, an increase or decrease of the emission intensity as schematically shown in Figure 56(a). Under a stationary excitation shown in Figure 56(b), the stimulation enhances and the quenching reduces the emission intensity temporarily.

These phenomena are utilized for IR detection and radiographic imaging, in which the intensity of the stimulated emission is used to measure the intensity of IR light or X-rays (see 7.4).

Photostimulation is caused by the radiative recombination of the electrons (holes) released by photoactivation from deep trap levels, as shown in Figure 57(a). On the other hand, photoquenching is caused by the nonradiative recombination of holes (electrons) photoactivated from luminescent centers as shown in Figure 57(b). Figure 58 depicts the configuration coordinate model of photostimulation. The activation energy ϵ_0 of photostimulation is not generally equal to the thermal activation energy ϵ_t of trapped electrons discussed before with reference to Figure 49. Since the optical absorption process takes place in a very short time period without changing the configuration of the atoms in the center at that moment, the process is represented by the straight vertical transition in Figure 58 from state III (a trap or the quasi-stable state of emitting centers) to state II (the conduction band or emitting centers). On the other hand, the thermal activation needs energy ϵ_t to overcome at least the lowest barrier between states II and III in Figure 58; hence, the activation energy ϵ_t is generally smaller than ϵ_0 . Photostimulation spectra (i.e., excitation spectra for IR stimulation) can be used to measure the optical activation energy ϵ_0 .

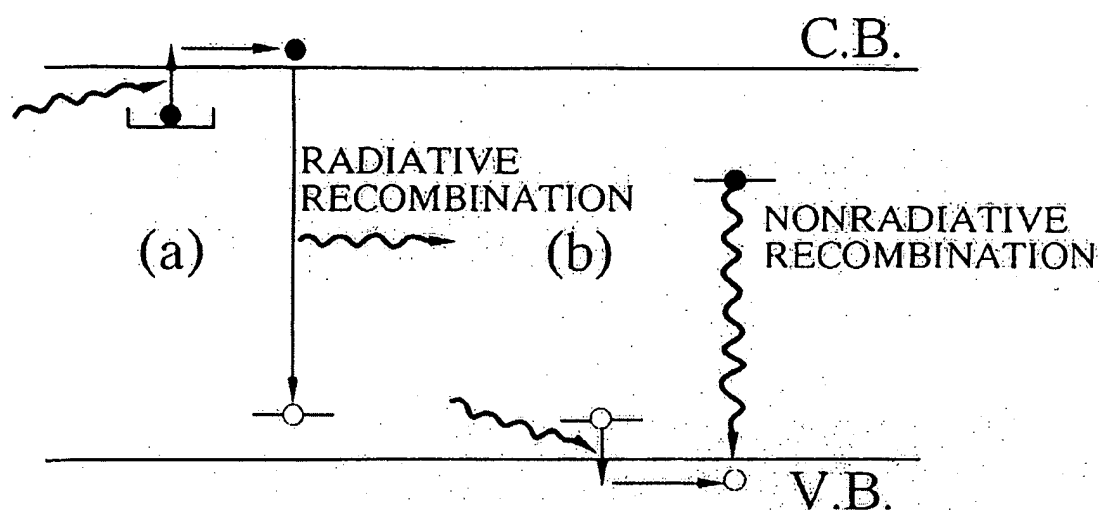


Figure 57 Photostimulation process (a), and photoquenching process (b) in an energy band scheme. C.B. and V.B. indicate the conduction band and the valence band of the host crystal, respectively.

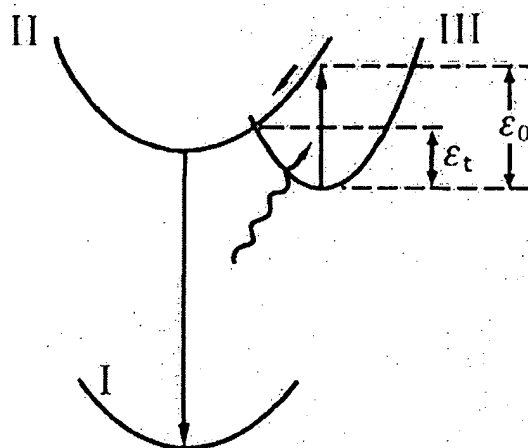


Figure 58 Photostimulation in configurational coordinate models.

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